



## Short communication

Preparation of  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  solid electrolyte from *N*-methylformamide solution and application for all-solid-state lithium battery

Shingo Teragawa, Keigo Aso, Kiyoharu Tadanaga, Akitoshi Hayashi, Masahiro Tatsumisago\*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

## HIGHLIGHTS

- $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  solid electrolytes (SE) were prepared from *N*-methylformamide solution.
- $\text{LiCoO}_2$  was coated with  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  SE by using the solution.
- SE-coated  $\text{LiCoO}_2$  exhibited a reversible capacity in all-solid-state batteries.

## ARTICLE INFO

## Article history:

Received 30 August 2013

Received in revised form

26 September 2013

Accepted 28 September 2013

Available online 5 October 2013

## Keywords:

All-solid-state battery

Lithium secondary battery

Sulfide solid electrolyte

Liquid phase method

Composite electrode

## ABSTRACT

Electrode–solid electrolyte composite materials for all-solid-state lithium batteries were prepared by coating of the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  solid electrolyte onto  $\text{LiCoO}_2$  particles using a *N*-methylformamide (NMF) solution of 80 $\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$  (mol%) solid electrolyte. SEM and EDX analysis showed that the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  solid electrolyte was uniformly coated on  $\text{LiCoO}_2$  particles. The all-solid-state cell using the  $\text{LiCoO}_2$  particles coated with the solid electrolyte showed higher charge–discharge capacity than the cells using uncoated  $\text{LiCoO}_2$  particles.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Lithium secondary batteries have been used extensively for power sources of various portable electric devices because of their high-energy density [1]. Lithium secondary batteries have also been considered as power sources for electric vehicles and hybrid electric vehicles, which require safe batteries with high capacity. However, commercialized lithium-ion batteries have an obvious limitation in safety because organic liquid electrolytes have risks for leakage and flammability.

All-solid-state lithium secondary batteries with inorganic solid electrolytes (SEs) have been attracting attention for its advantages for safety and reliability [2]. Thus, interests of solid electrolytes with high lithium-ion conductivities have been increasing. Recently, Kanno et al. have reported that  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  crystals

showed extremely high lithium-ion conductivity of over  $10^{-2} \text{ S cm}^{-1}$  at room temperature [3]. In addition, crystalline phases and lithium-ion conductivities of binary  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  systems have been studied [4,5]. We have reported that  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glass–ceramics shows high lithium-ion conductivities of over  $10^{-3} \text{ S cm}^{-1}$  at room temperature [6,7], and we also have reported that all-solid-state cells with the glass–ceramics solid electrolyte worked reversibly [8].

In addition to the development of solid electrolytes with high lithium-ion conductivities, formation of intimate electrode–solid electrolyte interfaces in the bulk-type all-solid-state battery system is very important to realize high performance of all-solid-state batteries [9–11]. As an example, all-solid-state cells using  $\text{LiCoO}_2$  particles coated with  $\text{Li}_2\text{SiO}_3$  showed a high power density [12]. In order to form intimate electrode–solid electrolyte interfaces, we have reported the coating of  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  solid electrolyte on  $\text{LiCoO}_2$  particles (SE-coated  $\text{LiCoO}_2$ ) by the pulse laser deposition (PLD) method [9,11]. Charge–discharge capacities of all-solid-state cells using the SE-coated  $\text{LiCoO}_2$  particles were higher than those of cells with uncoated  $\text{LiCoO}_2$ .

\* Corresponding author. Tel./fax: +81 72 2549331.

E-mail address: [tatsu@chem.osakafu-u.ac.jp](mailto:tatsu@chem.osakafu-u.ac.jp) (M. Tatsumisago).

Preparation of solid electrolytes from liquid phase instead of gas-phase methods must be a very simple and effective process to form good electrode–electrolyte interfaces. Favorable solid–liquid interfaces are easily formed between electrodes and solutions of solid electrolytes, and the intimate solid–solid interfaces between electrodes and solid electrolytes can be achieved by removing solvents. Very recently, preparation of the  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$  thin film by a solution process using a hydrazine-based solvent has been reported [13], and we have reported that  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$  solid electrolytes were prepared from *N*-methylformamide (NMF) solution of the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  (mol%) solid electrolyte [14]. NMF is known to dissolve some materials containing  $\text{PS}_4^{3-}$  groups or  $\text{P}_2\text{S}_6$  ethane-like groups [15,16], and it has lower toxicity than hydrazine.

In the present study,  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$  solid electrolyte was coated on  $\text{LiCoO}_2$  particles by using the NMF solution of the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  electrolyte to form electrode–electrolyte composite materials. All-solid-state cells using the SE-coated  $\text{LiCoO}_2$  particles were fabricated and their battery performance was evaluated.

## 2. Experimental

Sulfide-based solid electrolyte was coated on  $\text{LiCoO}_2$  particles using a *N*-methylformamide (NMF) solution of the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  (mol%) glass electrolyte. The  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass was prepared by the mechanical milling method. Reagent-grade  $\text{Li}_2\text{S}$  (Idemitsu Kosan, 99.9%) and  $\text{P}_2\text{S}_5$  (Aldrich, 99%) crystalline powders were used as starting materials. A mixture of these materials was mechanically milled at room temperature by a planetary ball mill apparatus (Fritsch, Pulverisette 7) using a zirconia pot (volume 45 mL) with 500 zirconia balls (4 mm in diameter). A rotating speed was 510 rpm and a milling time was 8 h. The  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass electrolyte was dissolved into NMF and a homogeneous yellow solution was prepared (Fig. 1). The concentration of the NMF solution of solid electrolyte was 10 wt%. The NMF solution was mixed with  $\text{LiCoO}_2$  particles (D-10, Toda Kogyo Corp.) and dried at  $150^\circ\text{C}$  for 3 h under vacuum to remove NMF. The weight ratio of  $\text{LiCoO}_2$  to dissolved SE was  $\text{LiCoO}_2\text{:SE} = 92.5\text{:}7.5$ . The  $\text{LiCoO}_2$  particles used in this study were coated with  $\text{LiNbO}_3$  film in advance because all-solid-state cells using  $\text{LiCoO}_2$  particles coated with oxides such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [17],  $\text{LiNbO}_3$  [18] or  $\text{Li}_2\text{SiO}_3$  [12] showed a high power density. All processes including the mechanical milling were performed in a dry argon atmosphere.

Temperature dependence of ionic conductivity of the powders obtained from the NMF solution was measured by the AC impedance using an impedance analyzer (Solartron, 1260) in the frequency range of 1 Hz to 1 MHz. A pelletized sample with 10 mm in

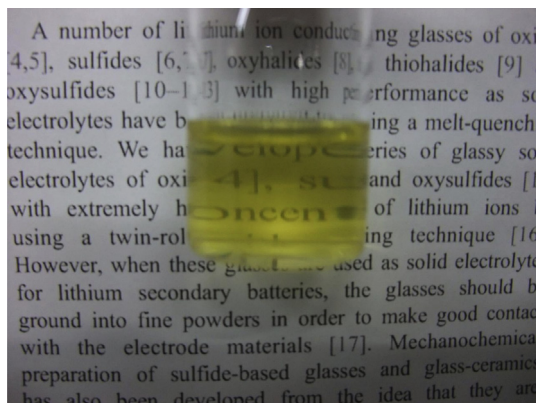


Fig. 1. *N*-Methylformamide solution of the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass electrolyte. The concentration of the solution was 10 wt%.

diameter and about 1 mm in thickness was used for the measurements. Carbon paste was applied to both faces of the pellet as a current collector. All measurements were performed in a dry argon atmosphere.

Morphology of  $\text{LiCoO}_2$  particles was observed using a scanning electron microscope (SEM, JSM-6610A, JEOL) equipped with an energy dispersive X-ray spectroscopy system (EDX, JED-2300, JEOL). All-solid-state cells ( $\text{In}/80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic solid electrolyte/ $\text{LiCoO}_2$ ) were constructed as follows to investigate their electrochemical performance. The  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  (mol%) glass–ceramic electrolyte was used as a separator layer. The  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic electrolyte was prepared by the mechanical milling method and subsequent heat treatment [6]. Surface coated  $\text{LiCoO}_2$  with solid electrolytes (SE-coated  $\text{LiCoO}_2$ ) and the glass–ceramic electrolyte were mixed using a mortar to prepare composite positive electrodes; the weight ratio of  $\text{LiCoO}_2\text{:SE-coatings}$  is 92.5:7.5 and that of  $\text{LiCoO}_2\text{:SE}$  (coating layer + glass–ceramic) is 70:30. Indium foil (Furuuchi Chem., 99.999%; 0.1 mm thickness) was used as a negative electrode. A bilayer pellet (10 mm in diameter) consisting of the composite electrode (10 mg) and the glass–ceramic electrolyte as a separator layer (80 mg) was prepared by pressing under 360 MPa, and then the indium foil was attached to the pellet by pressing under 240 MPa. The all-solid-state cells were charged and discharged using a charge–discharge measuring device (BTS-2004; Nagano Co., Ltd.) at room temperature in an Ar atmosphere.

## 3. Results and discussion

Fig. 2 shows the temperature dependence of ionic conductivity of a pelletized solid electrolyte obtained from the NMF solution. Although the conductivity at  $25^\circ\text{C}$  was previously measured for the solid electrolyte [14], activation energy for conduction of the electrolyte has not been reported. Ionic conductivity of the solid electrolyte was  $2.6 \times 10^{-6} \text{ S cm}^{-1}$  at room temperature. The ionic conductivity obeyed the Arrhenius law; the activation energy for the ionic conduction calculated from the slope of the plots was  $42 \text{ kJ mol}^{-1}$ . The ionic conductivity of the solid electrolyte obtained from the NMF solution was lower than that of the original  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass ( $1.7 \times 10^{-4} \text{ S cm}^{-1}$ ) [6,19], and the activation energy was higher than that of original  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass ( $37 \text{ kJ mol}^{-1}$ ) [19]. The lower conductivity was caused by crystallization of  $\text{Li}_3\text{PS}_4$  and  $\text{Li}_2\text{S}$  with low conductivity [14]. Although

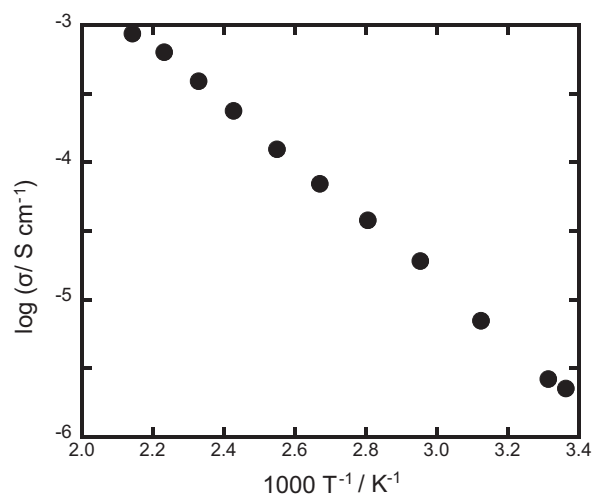


Fig. 2. Temperature dependence of ionic conductivity of the solid electrolyte obtained from the NMF solution.

ionic conductivity of the solid electrolyte prepared from the NMF solution was lower than that of original  $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$  glass, the conductivity was higher than that of the  $\text{Li}_3\text{PS}_4$  crystal ( $10^{-7} \text{ S cm}^{-1}$ ) [5]. This suggests that a glass phase with higher conductivity partially exists in the prepared electrolyte.

Fig. 3 shows the SEM and EDX mapping (Co, P and S) images of the  $\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5$  solid-electrolyte-coated (SE-coated)  $\text{LiCoO}_2$  particles. The SEM image showed that the particle size of the  $\text{LiCoO}_2$  particles was about  $20 \mu\text{m}$ ; the coating materials were observed on the  $\text{LiCoO}_2$  particles. The particle size of  $\text{LiCoO}_2$  was not changed by coating. Phosphorous and sulfur elements of  $\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5$  SE film were detected on  $\text{LiCoO}_2$  particles, indicating that the  $\text{LiCoO}_2$  particles were covered with  $\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5$  SE film. The thickness of SE on the  $\text{LiCoO}_2$  was calculated from the surface area of  $\text{LiCoO}_2$  ( $0.12 \text{ m}^2 \text{ g}^{-1}$ ) and density of  $\text{Li}_3\text{PS}_4$  crystals ( $1.872 \text{ g cm}^{-3}$ ) [20]. The estimated thickness of SE layers was about  $360 \text{ nm}$ .

All-solid-state cells using the prepared SE-coated  $\text{LiCoO}_2$  ( $\text{LiCoO}_2\text{:SE-film} = 92.5\text{:}7.5$ , wt.%) or uncoated  $\text{LiCoO}_2$  as a positive electrode material were fabricated. Fig. 4 shows the initial charge–discharge curves (A) and cycle performance (B) of the all-solid-state  $\text{In/LiCoO}_2$  cells with SE-coated  $\text{LiCoO}_2$  (a) or uncoated  $\text{LiCoO}_2$  (b).  $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$  glass–ceramic electrolyte was added to positive electrode layers of both cells, and conductive additives such as acetylene black were not added in this study. The weight ratio of  $\text{LiCoO}_2$  to SE including the coating layer was  $\text{LiCoO}_2\text{:SE} = 70\text{:}30$ . This weight ratio was the same as that of the cell using uncoated- $\text{LiCoO}_2$ . The cells were charged up to  $3.6 \text{ V}$  (vs.  $\text{Li-In}$ ) and discharged to  $2 \text{ V}$  (vs.  $\text{Li-In}$ ) at a current density of  $0.13 \text{ mA cm}^{-2}$ . The reversible capacity of the cells using uncoated  $\text{LiCoO}_2$  (b) was  $96 \text{ mAh g}^{-1}$ , and that of the cell using SE-coated  $\text{LiCoO}_2$  (a) was  $107 \text{ mAh g}^{-1}$ . These capacities were normalized by the mass of  $\text{LiCoO}_2$  active material. The reversible capacity of the cell (a) was higher than that of the cell (b), and cycle performance of the cell (a) was almost the same or better than that of the cell (b). Although the ionic conductivity of the solid electrolyte obtained from the NMF solution was relatively low at the present stage, the capacity of the all-solid-state cell was increased by the formation of intimate electrode–electrolyte interfaces.

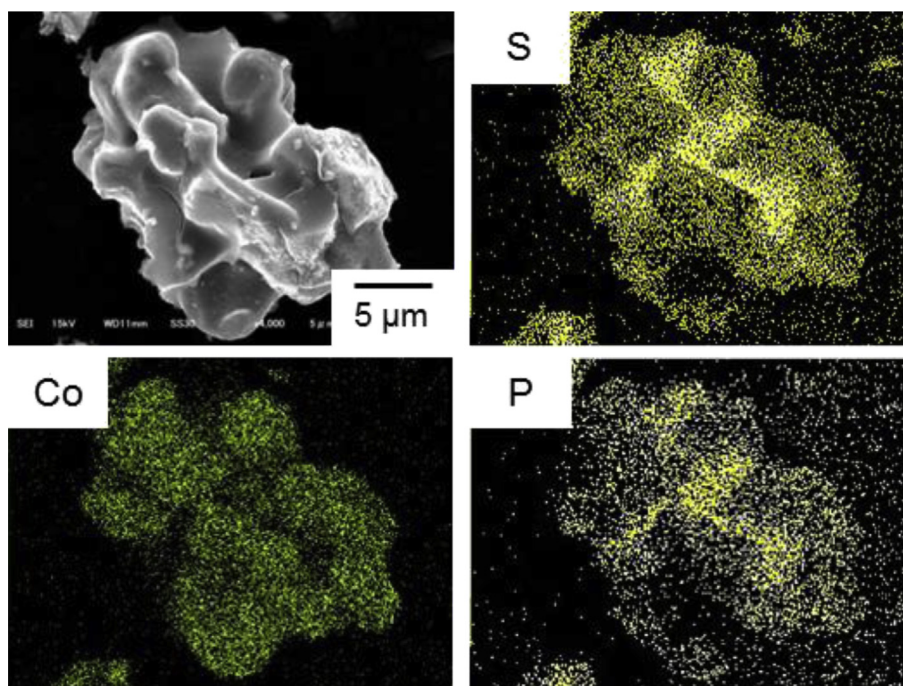


Fig. 3. SEM and EDX mapping (Co, P and S) images of SE-coated  $\text{LiCoO}_2$  particles.

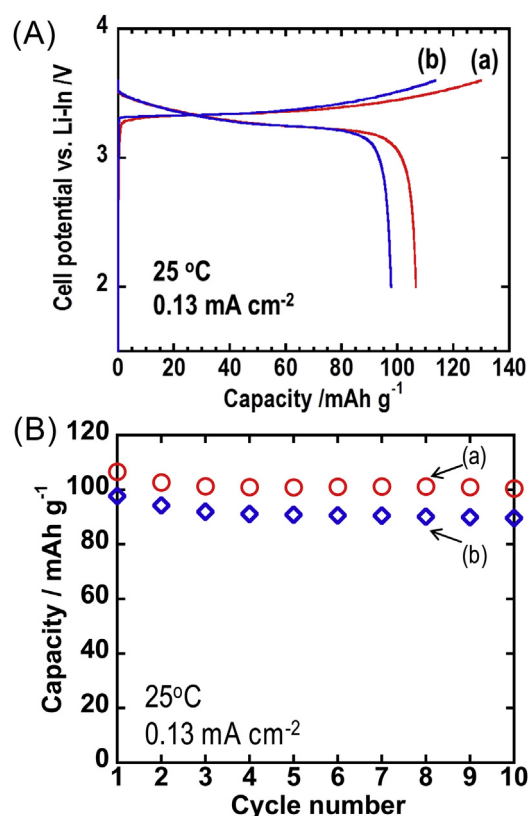


Fig. 4. Initial charge–discharge curves (A) and cycle performances (B) of the all-solid-state cells using SE-coated  $\text{LiCoO}_2$  (a) and uncoated  $\text{LiCoO}_2$  (b).

The ionic conductivity of the  $\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5$  solid electrolyte obtained from the NMF solution was lower than that of the solid electrolyte prepared by the pulsed laser deposition technique [11]. The performance of all-solid-state cells will be improved with the increasing ionic conductivity of solid electrolytes. Future studies

about electrolyte composition and solvent are needed to increase of ionic conductivities of solid electrolytes via liquid phase.

#### 4. Conclusions

The  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  solid electrolyte was prepared from *N*-methylformamide (NMF) solution of the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass electrolyte. The ionic conductivity of the prepared electrolyte was  $2.6 \times 10^{-6} \text{ S cm}^{-1}$  at room temperature, and the activation energy for conduction was  $42 \text{ kJ mol}^{-1}$ . The  $\text{LiCoO}_2$  particles were coated with the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  solid electrolyte via the NMF solution of the glass electrolyte. The all-solid-state cell using the SE-coated  $\text{LiCoO}_2$  particles as the electrode material showed a higher charge–discharge capacity than the cell using uncoated  $\text{LiCoO}_2$  particles, suggesting that the intimate electrode–solid electrolyte interfaces were formed by the use of the electrolyte solution.

#### Acknowledgment

This research has been financially supported by the Japan Science and Technology Agency (JST), Core Research for Evolutional Science and Technology (CREST) project, and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

#### References

- [1] J.-M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
- [2] K. Takada, *Acta Mater.* 61 (2013) 759–770.
- [3] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, *Nat. Mater.* 10 (2011) 682–686.
- [4] M. Tachez, J.-P. Malugani, R. Mercier, G. Robert, *Solid State Ionics* 14 (1984) 181–185.
- [5] K. Homma, M. Yonemura, T. Kobayashi, M. Nagao, M. Hirayama, R. Kanno, *Solid State Ionics* 182 (2011) 53–58.
- [6] A. Hayashi, S. Hama, T. Minami, M. Tatsumisago, *Electrochem. Commun.* 5 (2003) 111–114.
- [7] F. Mizuno, A. Hayashi, K. Tadanaga, M. Tatsumisago, *Adv. Mater.* 17 (2005) 918–921.
- [8] F. Mizuno, S. Hama, A. Hayashi, S. Hama, K. Tadanaga, T. Minami, M. Tatsumisago, *Chem. Lett.* 12 (2002) 1244–1245.
- [9] A. Sakuda, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, *Electrochem. Solid State Lett.* 13 (2010) A73–A75.
- [10] H. Kitaura, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, *J. Mater. Chem.* 21 (2011) 118–124.
- [11] A. Sakuda, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, *J. Power Sources* 196 (2011) 6735–6741.
- [12] A. Sakuda, H. Kitaura, A. Hayashi, K. Tadanaga, M. Tatsumisago, *Electrochem. Solid State Lett.* 11 (2008) A1–A3.
- [13] Y. Wang, Z. Liu, X. Zhu, Y. Tang, F. Huang, *J. Power Sources* 224 (2013) 225–229.
- [14] S. Teragawa, K. Aso, K. Tadanaga, A. Hayashi, M. Tatsumisago, *Chem. Lett.* (2013), <http://dx.doi.org/10.1246/cl.130726>.
- [15] S. Coste, J. Hanko, M. Bujoli-Doeuff, G. Louarn, M. Evain, R. Brec, B. Alonso, S. Jobic, M.G. Kanatzidis, *J. Solid State Chem.* 175 (2003) 133–145.
- [16] S. Coste, E. Gautier, M. Evain, M. Bujoli-Doeuff, R. Brec, S. Jobic, M.G. Kanatzidis, *Chem. Mater.* 15 (2003) 2323–2327.
- [17] N. Ohta, K. Takada, L. Zhang, R. Ma, M. Osada, T. Sasaki, *Adv. Mater.* 18 (2006) 2226–2229.
- [18] N. Ohta, K. Takada, I. Sakaguchi, L. Zhang, R. Ma, K. Fukuda, M. Osada, T. Sasaki, *Electrochem. Commun.* 9 (2007) 1486–1490.
- [19] M. Tatsumisago, S. Hama, A. Hayashi, H. Morimoto, T. Minami, *Solid State Ionics* 154–155 (2002) 635–640.
- [20] R. Mercier, J.-P. Malugani, B. Fahys, G. Robert, *Acta Crystallogr. Sect. B Struct. Sci.* B38 (1982) 1887–1890.